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# $TiO_2$–UV photocatalytic oxidation of Reactive Yellow 14: Effect of operational parameters

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**Abstract**

The photocatalytic decolourisation and degradation of an azo dye Reactive Yellow (RY14) in aqueous solution with $TiO_2$ as photocatalyst in slurry form has been carried out using UV-A radiation (365 nm). The effect of various parameters such as catalyst loading, radiation intensity and initial dye concentration on the dye removal was investigated to find optimum conditions. The decolourisation and degradation kinetics have been analysed. Both follow modified Langmuir–Hinshelwood kinetic (L–H) model. A study on the effect of electron acceptors on photooxidation reveals that both decolourisation and degradation increase in the presence of $H_2O_2$, $(NH_4)_2S_2O_8$, $KBrO_3$, to certain dosage beyond which the enhancement effect is negligible. But negative effects are observed in the presence of NaCl or $Na_2CO_3$.
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*Keywords:* AOP; $TiO_2$; Azodyes; Reactive Yellow 14; UV radiation; Electron acceptors

## 1. Introduction

Wastewaters from textile and dye industries are highly coloured with significant amount of auxiliary chemicals. The discharge of these wastewater introduced intensive colour and toxicity to aquatic environment causing serious environmental problems [1]. Reactive dyes are widely used in the textile industries because of its simple dyeing procedure and good stability during washing process [2]. Due to the complex aromatic structure and stability of these dyes, conventional biological treatment methods are ineffective for degradation [3]. Hence, the concentration remains constant in the environment. A number of physical and chemical techniques had been reported for the treatment of dye effluents. Among these the advanced oxidation process (AOPs) are more efficient as they are capable of mineralising a wide range of organic pollutants.

In recent years AOPs have been developed to meet the increasing need of effective wastewater treatment. AOP generates powerful oxidising agent (hydroxyl radicals). Heterogeneous photocatalysis through illumination of UV on semiconductor surface is an attractive advanced oxidation process. The photocatalyst titanium dioxide ($TiO_2$) is a wide band gap semiconductor (3.2 eV) and is successfully used as a photocatalyst for the treatment of organic [4,5] and dye pollutants [6–9]. In our earlier work we have reported the photocatalytic degradation of Reactive Orange 4 by various AOPs using UV and solar light [10–13].

For practical application of dye wastewater treatment by $TiO_2$–UV process, there is a need to determine the optimal conditions of experimental parameters for economic removal of the dye. In the present investigation we have undertaken a reactive class mono azo dye Reactive Yellow 14 and examined the various parameters to find out the optimum conditions for removal of colour and aromatic part of the dye.

## 2. Experimental

### 2.1. Material

Reactive Yellow 14 dye (85% purity), obtained from Colour Chem Pondicherry was used as received. A gift sample of $TiO_2$-P25 was received from Degussa (Frankfurt, Germany). $TiO_2$-P25 contains anatase 80% and rutile 20% with the mean particle size of 30 nm and a BET surface area of 50 $m^2/g$. ZnO has a

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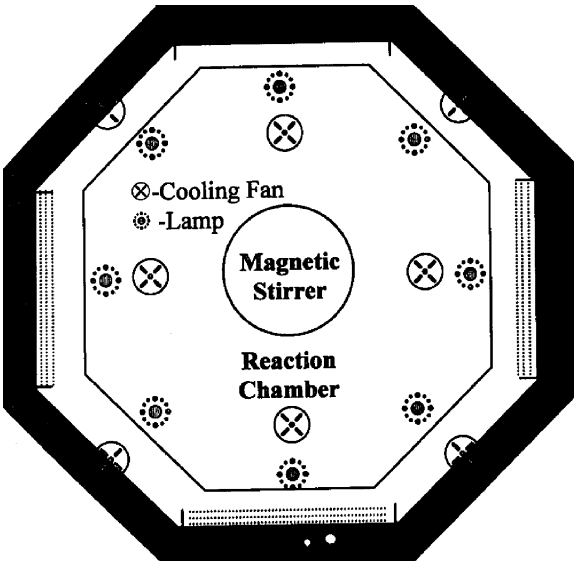


Fig. 1. Schematic diagram of photoreactor.

particle size 0.1–4 μm and surface area 10 $m^2$/g. $TiO_2$ (anatase) received from Aldrich Chemical Company has a medium particle size of approximately 1 μm with a specific surface area of 8.9 $m^2$/g. The other chemicals CdS, $Fe_2O_3$ and $SnO_2$ (s.d. Fine). AnalaR grade $H_2O_2$ (30%, w/w), $(NH_4)_2$ $S_2O_8$ and $KBrO_3$ (Merck) were used as such. The double distilled water was used to prepare experimental solutions. The natural pH of the aqueous dye solution is 5.5. The pH of the solutions was adjusted using $H_2SO_4$ or NaOH.

### 2.2. Apparatus

Heber multilamp photoreactor model HML-MP 88 (Fig. 1) was used for photoreaction. This model consists of eight medium pressure mercury vapour lamps of 8 W set in parallel. The lamp emits in a broad spectrum and emitting at 365 nm of peak wavelengths. It has a reaction chamber with specially designed reflectors made of highly polished aluminium and built in cooling fan at the bottom. It is provided with the magnetic stirrer at the centre. Open borosilicate glass tube of 50 ml capacity, 40 cm height and 20 mm diameter was used as a reaction vessel with the total radiation exposure length of 330 mm. The irradiation was carried out using four parallel medium pressure mercury lamps (32 W) in open-air condition. The light intensity was measured using ferrioxalate actinometer and the intensity was found to be $1.381 \times 10^{-6}$ einstein/min. The solution with $TiO_2$ and dye was continuously aerated by a pump to provide oxygen and for complete mixing of reaction solution.

### 2.3. Procedure

In all cases 50 ml of the dye solution containing appropriate quantity of the $TiO_2$ suspensions were used. The suspension was stirred for 30 min in the dark for the attainment of adsorption equilibrium. At specific time intervals 2 ml of the sample was withdrawn and centrifuged to separate the catalyst. One milliliter of the centrifugate was diluted to 10 ml and its absorbance at 410 and 254 nm were measured. The absorbance at 410 nm is due to colour of the dye solution and it is used to monitor the decolourisation of dye. The absorbance at 254 nm represents the aromatic content of RY14 and the decrease of absorbance at 254 nm indicates the degradation of aromatic ring. Reactive Yellow 14 azo dye (RY14) (C.I. No. 19036, molecular formula = $C_{20}H_{19}N_4O_{11}S_3Na_2Cl$, molecular weight = 669.00) is extensively used in dyeing industries. The chemical structure of the dye is given in Fig. 2.

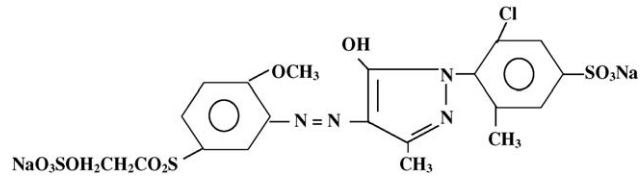


Fig. 2. Chemical structure of RY14 dye.

UV spectral analysis was done using Hitachi U-2001 spectrophotometer. The pH of the solution is measured by using HANNA Phep (Model H 198107) digital pH meter.

## 3. Results and discussions

### 3.1. Photocatalytic oxidation experiments

Photocatalytic experiments were carried out under the following conditions: (i) dye solution with the UV in the absence of $TiO_2$, (ii) dye solution with $TiO_2$ in dark and (iii) dye solution under irradiation of UV radiation with $TiO_2$, the results are shown in Fig. 3. Dye is resistant to self-photolysis in UV radiation. After 30 min of magnetic stirring in the presence of photocatalyst without UV irradiation, about 22% decrease in concentration was observed from absorbance measurements. This is due to the adsorption of dye molecule on the surface of $TiO_2$-P25. The irradiation with the catalysts caused 98.7%, of decolourisation and 84.2%, of degradation after 60 min. This shows that the dye can be effectively decolourised and degraded by UV radiation using $TiO_2$-P25. Fig. 4 shows the changes in

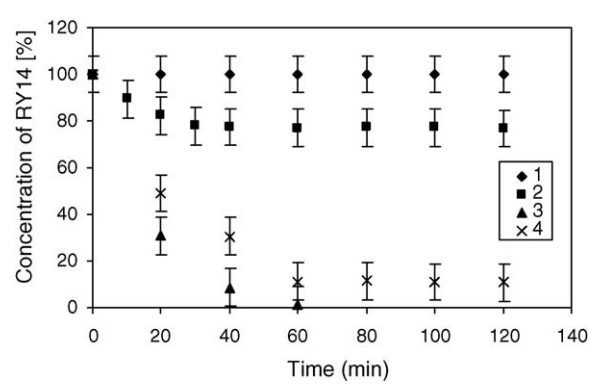


Fig. 3. Photodegradability of RY14 by UV/$TiO_2$-P25. $TiO_2$-P25 = 4 g/l, [RY14] = $5 \times 10^{-4}$ mol/l, pH 5.5 ± 0.1. Dye solution irradiated with UV radiation in the absence of $TiO_2$-P25 (1), dye solution treated with $TiO_2$-P25 in dark (2) and dye solution irradiated with UV radiation in the presence of $TiO_2$-P25 (3 and 4); (3) decolourisation and (4) degradation.

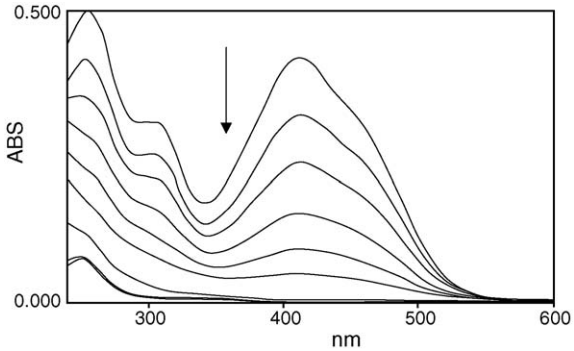


Fig. 4. The changes in UV–vis spectrum on irradiation by means of UV radiation of an aqueous suspension of $TiO_2$ containing RY14. $TiO_2 = 4$ g/l, $[RY14] = 5 \times 10^{-4}$ mol/l, pH 5.5.

the optical densities of RY14 at 410 and 254 nm under different irradiation times. The fast decolourisation of dye is due to the initial electrophilic cleavage of its chromophoric azo (–N=N–) bond. Azo bonds are more active in these dyes and they are oxidised by positive hole, hydroxyl radical and reduced by electron in the conduction band [14]. RY14 contains one azo bond and decolourisation of RY14 showed that the chromophoric, azo bond of dye molecule is destroyed. The degradation of aromatic part of the dye molecule produced a number of intermediate compounds and removal of these intermediates took longer time. The degradation of aromatic part of the dye molecule was not complete. Only 90% of the dye was removed even after 15 h of irradiation. This shows that some of the intermediates produced are resistant to photocatalytic oxidation reaction.

### 3.2. Photodegradation efficiency of other photocatalysts

The photooxidation by other photocatalysts such as $TiO_2$ anatase, ZnO, $SnO_2$, CdS and $Fe_2O_3$ has been investigated. $SnO_2$, $Fe_2O_3$ and CdS have negligible activity on RY14 decolourisation and degradation and hence they are not shown in Fig. 5. $TiO_2$-P25 and ZnO are found to be more efficient when compared to $TiO_2$ anatase as shown in Fig. 5. The decolourisation efficiencies of $TiO_2$-P25, ZnO and $TiO_2$ anatase are 91.3, 98.9 and 57.4%, respectively, at the time of 40 min. At the same time the degradation efficiencies of these catalysts are 69.5, 83.1 and 21.8%. Generally semiconductors having large band gap have strong photocatalytic activities, $TiO_2$ and ZnO have band gap of 3.2 eV and show strong photocatalytic activity. The order of activities of the photocatalysts are ZnO > $TiO_2$-P25 > $TiO_2$ anatase in both processes. ZnO is found to be more efficient than $TiO_2$-P25 and $TiO_2$ anatase. The higher efficiency of ZnO than $TiO_2$ has also been reported in the treatment of pulp mill bleaching wastewater [15,16] and dye wastewater [17,18]. Kormann et al. [19] stated that the quantum yield of $H_2O_2$ production in illuminated aqueous suspensions of ZnO was found to be one order of magnitude higher than the corresponding value for $TiO_2$. In the case of $TiO_2$ anatase the decolourisation and degradation proceeds with lower efficiencies compared with $TiO_2$-P25. The photocatalytic activity of semiconductors is also dependent on the crystallinity, particle size, surface area and concentration of the impurities in the catalysts. The high photoreactivity of $TiO_2$-P25 over $TiO_2$ anatase is due to slow recombination of electron–hole pair and large surface area of $TiO_2$-P25.The surface area of $TiO_2$-P25 is six times higher than $TiO_2$ anatase. ZnO has the disadvantage of undergoing photocorrosion under acidic condition on illumination. Since band gap of $SnO_2$ is 3.87 eV, the UV (365 nm) radiation energy is not sufficient to activate the catalyst. CdS and $Fe_2O_3$ have smaller band gap (2.4 and 2.3 eV). The smaller band gap permits rapid recombination of electron–hole and so conduction band electron in these semiconductors cannot move into the electron acceptors in the solution rapidly. Hence, a negligible photocatalytic activity for decolourisation and degradation is observed in these catalysts. In the present study, $TiO_2$-P25 was chosen because of its high photocatalytic activity, higher surface area, resistance to photo corrosion, biological immunity and its low cost.

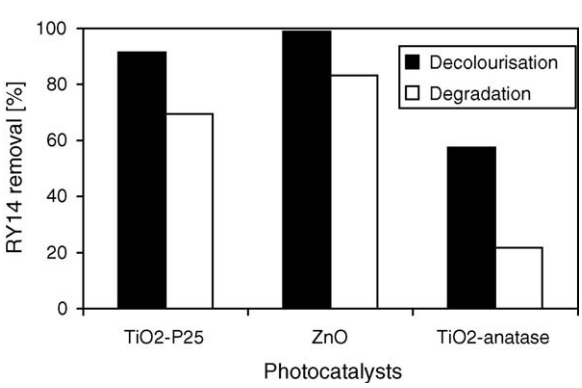


Fig. 5. Effect of various photocatalysts on decolourisation and degradation of RY14. $[RY14] = 5 \times 10^{-4}$, pH $7.0 \pm 0.1$, irradiation time = 40 min, amount of catalysts = 4 g/l.

### 3.3. Effect of $TiO_2$ dosage

The optimum amount of $TiO_2$ has to be added in order to avoid excess catalyst and also to ensure total absorption of radiation photons for efficient photodegradation. It depends on type of photocatalyst, pollutant concentration, characteristics of UV radiation (power, wavelength), photoreactor geometry, etc. [20]. Several authors have investigated the reaction rate as a function of catalyst loading in photocatalytic oxidation process [21,22]. The effect of photocatalyst ($TiO_2$) concentration on the degradation of RY14 was investigated from 1 to 6 g/l. The effect of $TiO_2$ loading on the initial rate of decolourisation and degradation is shown in Fig. 6. As the concentration of the catalyst is increased from 1 to 4 g/l the decolourisation increases from 52.6 to 91.3% and degradation from 36.0 to 69.5% at 40 min irradiation time. The enhancement of removal rate is due to: (i) the increase in the amount of catalyst weight which increases the number of dye molecule adsorbed and (ii) the increase in the density of particles in the area of illumination. Increase of the catalyst loading from 4 to 6 g/l makes the removal rate constant. By the addition of catalysts above 4 g/l the number of active sites on the $TiO_2$ surface may become almost constant because of the decreased radiation penetration, the increased radiation scattering and the loss in surface area by agglomeration. These reduce the specific activity

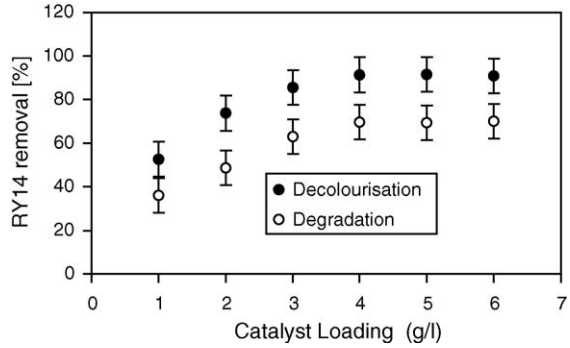


Fig. 6. Effect of catalyst loading on the decolourisation and degradation of RY14. [RY14] = 5 × $10^{-4}$ mol/l, pH 5.5 ± 0.1, irradiation time = 40 min.

of the catalyst. Bekbolet and Ozkosemen [23] found that 4 g/l of $TiO_2$ was the optimum catalyst loading for efficient degradation and stated that above this concentration the suspended particles of $TiO_2$ block the UV-light passage and reduce the formation of electron–hole pairs and active sites. Garcia and Takashima [24] found that 8 g/l of $TiO_2$ loading was most efficient in degradation and mineralisation of imazaquin in UV radiation. Alhakimi et al. [25] reported that a catalyst loading of 3 g/l was found to be optimum for potassium hydrogen phthalate degradation using $TiO_2$ and solar light. From these results it is clear that the optimum catalyst loading is not common for all photocatalytic reaction and it is dependent on various experimental parameters. The optimum amount of catalyst loading is found to be 4 g/1 for the degradation and decolourisation of RY14. Hence, 4 g/l was used as the catalyst dosage for the photocatalytic reactions.

### 3.4. Effect of UV radiation intensity

The effect of UV radiation power on the decolourisation and degradation of RY14 is shown in Fig. 7. The figure clearly shows that the removal rate increases with increasing UV power. The increase of radiation intensity from 16 to 62 W increases the decolourisation from 35.9 to 87.9% at the time of 20 min and degradation from 26.5 to 59.4% at the same time. UV radiation intensity determines the amount of photon absorbed by the catalyst. With the increase of the UV power, the catalyst absorbs more photons producing more electron–hole pairs in the catalyst surface and this increases the hydroxyl radical concentration and consequently increases the removal rate. Earlier studies [26,27] on the effect of light intensity have shown the following relationship between degradation rate and intensity: (i) at low radiation intensities, the rate increases linearly with increasing radiation intensity, (ii) at intermediate radiation intensities the rate depends on the square root of the radiation intensity and (iii) at high radiation intensities, the rate is independent of radiation intensity. They have attributed this variation to the recombination of photogenerated electron–hole pairs under different radiation intensities. Our results reveals that the photooxidation increases between 16 and 32 W but the increase is not significant in the range of 32–48 W and it is independent of radiation intensity in the high radiation intensity range (48–64 W). In the present work, we have used 32 W radiation intensity as optimum for photooxidation.

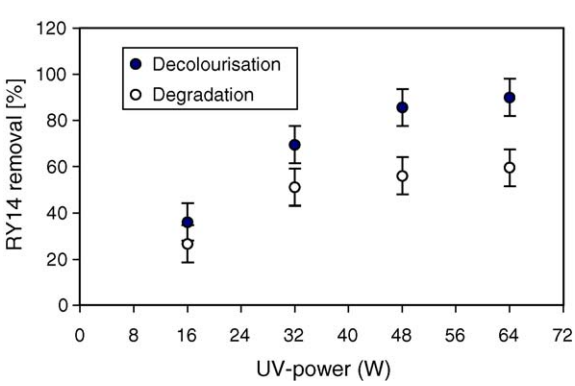


Fig. 7. Effect of UV radiation intensity on the decolourisation and degradation of RY14. [RY14] = 5 × $10^{-4}$ mol/l, pH 5.5 ± 0.1, irradiation time = 20 min.

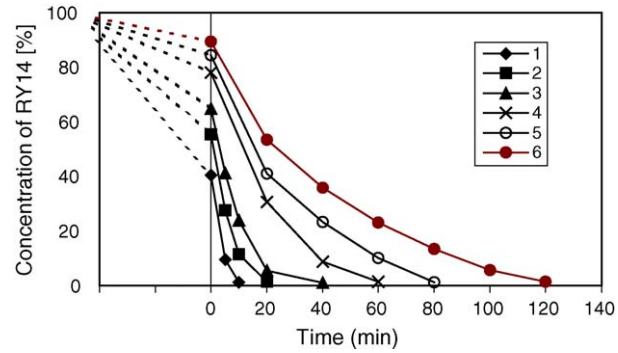


Fig. 8. Effect of initial dye concentrations on the decolourisation of RY14. $TiO_2$ = 4 g/l, pH 5.5 ± 0.1. [1] = 1 × $10^{-4}$ mol/l, [2] = 2 × $10^{-4}$ mol/l, [3] = 3 × $10^{-4}$ mol/l, [4] = 5 × $10^{-4}$ mol/l, [5] = 7 × $10^{-4}$ mol/l and [6] = 9 × $10^{-4}$ mol/l.

### 3.5. Effect of initial RY14 concentrations

The effect of various initial dye concentrations on the photocatalytic decolourisation and degradation of RY14 has been investigated from 1 to 9 × $10^{-4}$ mol/l. The results are shown in Figs. 8 and 9. Increase in the concentration of dye from 1 to 9 × $10^{-4}$ mol/l decreases the decolourisation from 100 to 46.6%, and degradation from 92.1 to 31.7%, in 20 min of UV irradia-

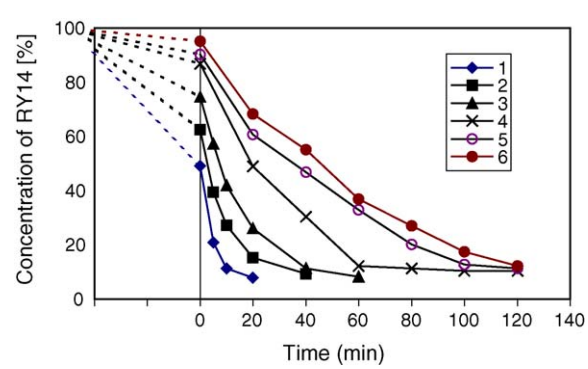


Fig. 9. Effect of initial dye concentrations on the degradation of RY14. $TiO_2$ = 4 g/l, pH 5.5 ± 0.1. [1] = 1 × $10^{-4}$ mol/l, [2] = 2 × $10^{-4}$ mol/l, [3] = 3 × $10^{-4}$ mol/l, [4] = 5 × $10^{-4}$ mol/l, [5] = 7 × $10^{-4}$ mol/l and [6] = 9 × $10^{-4}$ mol/l.

tion. With the increase in dye concentration, the time required for complete degradation increases. When the dye concentration increases the amount of dye adsorbed on the active sites per molecule of dye also increases. This affects the active sites of the catalysts hence decreases the efficiency of the $TiO_2$. An increase in dye concentration also decreases the path length of photon entering into the dye solution. At high dye concentration the dye molecules may absorb a significant amount of UV radiation rather than the catalyst and this may also reduce the catalytic efficiency.

### 3.6. Kinetics of photocatalytic degradation of RY14

The photocatalytic decolourisation and degradation of RY14 dye with $TiO_2$ obey apparently pseudo-first order kinetics at low initial dye concentration and the rate expression is given by Eq. (1).

$$\frac{-\mathrm{d}[C]}{\mathrm{d}t} = k'[C] \tag{1}$$

where $k'$ is the pseudo-first order rate constant. The dye is adsorbed on to $TiO_2$ surface and the adsorption–desorption equilibrium is reached in 30 min. After adsorption the equilibrium concentration of dye solution is taken as the initial dye concentration for kinetic analysis. Integration of the Eq. (1) (with the limit of $C = C_0$ at $t = 0$ with $C_0$ being the equilibrium concentration of the bulk solution) gives (2).

$$\ln\left[\frac{C_0}{C}\right] = k't \tag{2}$$

where $C_0$ is the equilibrium concentration of dye and $C$ is the concentration at time '$t$'.

A plot of $\ln C_0/C$ versus $t$ for decolourisation and degradation are shown in Figs. 10 and 11.The rate constants are reported in Table 1. A linear relation between dye concentration and irradiation time has been observed. Many authors [28–30] have used the modified Langmuir–Hinshelwood (L–H) kinetic expression to analyse the heterogeneous photocatalytic reaction successfully. The experimental data has been rationalised in terms of the modified form of L–H kinetic model to describe the solid–liquid

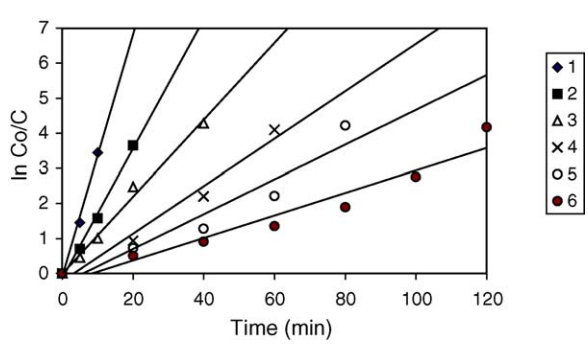


Fig. 10. Kinetics of RY14 decolourisation for different initial concentrations by UV/$TiO_2$-P25. $TiO_2$-P25 = 4 g/l, pH 5.5 ± 0.1. [1] = 1 × $10^{-4}$ mol/l, [2] = 2 × $10^{-4}$ mol/l, [3] = 3 × $10^{-4}$ mol/l, [4] = 5 × $10^{-4}$ mol/l, [5] = 7 × $10^{-4}$ mol/l and [6] = 9 × $10^{-4}$ mol/l.

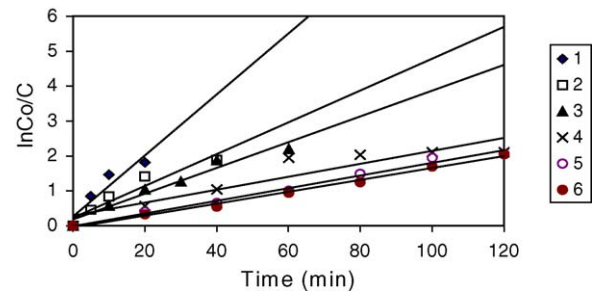


Fig. 11. Kinetics of RY14 degradation for different initial concentrations by UV/$TiO_2$-P25. $TiO_2$-P25 = 4 g/l, pH 5.5 ± 0.1. [1] = 1 × $10^{-4}$ mol/l, [2] = 2 × $10^{-4}$ mol/l, [3] = 3 × $10^{-4}$ mol/l, [4] = 5 × $10^{-4}$ mol/l, [5] = 7 × $10^{-4}$ mol/l and [6] = 9 × $10^{-4}$ mol/l.

reaction successfully. The rate of oxidation of RY14 dye at surface reaction is proportional to the surface coverage of dye on the $TiO_2$ assuming that the dye is strongly adsorbed on the catalyst surface than the intermediate products [31]. The effect of dye concentration on the rate of degradation is given in the form of Eqs. (3) and (4) [32].

$$r = \frac{K_1 K_2 C}{1 + K_1 C} \tag{3}$$

$$\frac{1}{r} = \frac{1}{K_1 K_2 C} + \frac{1}{K_2} \tag{4}$$

where $C$ is the concentration of the dye at time '$t$', $K_1$ the constant related to adsorption and $K_2$ is to the reaction properties of the dye. At low concentrations, i.e., concentrations up to 3 × $10^{-4}$ mol/l, the applicability of L–H equation for the decolourisation and degradation has been confirmed by the linear plot obtained by plotting reciprocal of initial rate ($1/r$) against reciprocal of initial concentration ($1/C$) as shown in Fig. 12. The values $K_1$ and $K_2$ are found to be 0.24 × $10^{-4}$ $M^{-1}$, 0.257 × $10^{-4}$ M $m^{-1}$ for decolourisation and 0.37 × $10^{-4}$ $M^{-1}$, 0.11 × $10^{-4}$ M $m^{-1}$ for degradation, respectively.

### 3.7. Effect of electron acceptors

In photocatalytic reaction of $TiO_2$ the major energy-wasting step is the electron–hole recombination, which leads to low quantum yield. Hence, the prevention of electron–hole recombination becomes very important. This can be achieved by adding proper electron acceptor to the system. Usually molecular oxy-

Table 1
Rate constants of RY14 decolourisation and degradation by UV/$TiO_2$-P25 process

| Initial concentration (×$10^{-4}$ mol/l) | Decolourisation $k'$ ($min^{-1}$) | Degradation $k'$ ($min^{-1}$) |
|---|---|---|
| 1 | 0.265 | 0.091 |
| 2 | 0.182 | 0.070 |
| 3 | 0.123 | 0.052 |
| 5 | 0.046 | 0.028 |
| 7 | 0.016 | 0.019 |
| 9 | 0.011 | 0.016 |

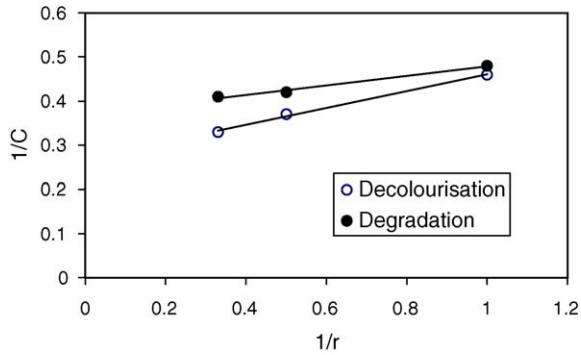


Fig. 12. Linearised reciprocal kinetic plot of the decolourisation and degradation of RY14 up to $3 \times 10^{-4}$ mol/l. $TiO_2$ = 4 g/l, pH 5.5 ± 0.1.

gen is used as an electron acceptor in heterogeneous photocatalysed reaction. Besides the addition of molecular oxygen, the electron–hole recombination can be reduced by the addition of irreversible electron acceptors such as $H_2O_2$, $S_2O_8^{2-}$ and $BrO_3^-$. Gratzel et al. [33] reported that rate-enhancing effects of the added inorganic oxidants such as $H_2O_2$, $IO_4^-$, $ClO_3^-$, $S_2O_8^{2-}$ on $TiO_2$ photocatalytic degradation of chlorophenol, 2,7-polychlorinateddibenzodioxin and atrazine. Pelizzeti et al. [34] also reported rate-enhancing effect of the added oxidants on $TiO_2$ catalysed degradation of organic compounds. The addition of these electron acceptors enhanced the degradation rate by several ways: (i) preventing the electron–hole recombination by accepting the conduction band electron, (ii) increasing the hydroxyl radical concentration and (iii) generating other oxidising species to accelerate the intermediate compound oxidation rate.

### 3.7.1. Effect of $H_2O_2$ addition

In order to keep the efficiency of the added $H_2O_2$, it is necessary to choose the optimum concentration of $H_2O_2$ according to the type and concentration of the pollutants. The effect of addition of $H_2O_2$ (5–25 mM) on the photocatalytic oxidation is shown in Fig. 13. The addition of $H_2O_2$ from 5 to 15 mM increases the decolourisation from 84.9 to 90.4% and degradation from 58.2 to 64.3% in 20 min. When the $H_2O_2$ concentration is higher than 15 mM no increase in oxidation rate of RY14 was

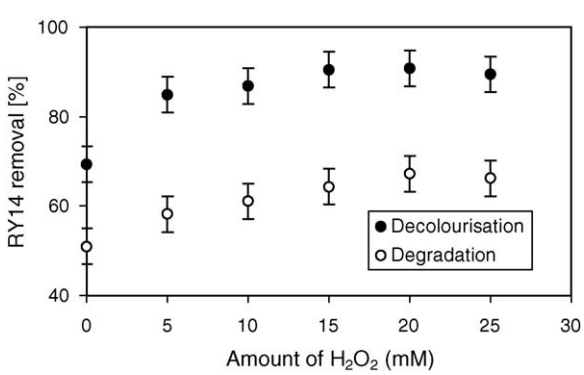


Fig. 13. Effect of $H_2O_2$ addition on the decolourisation and degradation of RY14. $TiO_2$-P25 = 4 g/l, [RY14] = $5 \times 10^{-4}$ mol/l, pH 5.5 ± 0.1, irradiation time = 20 min.

observed. Hence, 15 mM $H_2O_2$ concentration appears to be optimal for the degradation. The enhancement of decolourisation and degradation by addition of $H_2O_2$ is due to increase in the hydroxyl radical concentration by the following ways:

(i) Oxygen is the primary acceptor of the conduction band electron with formation of super oxide radical anion (Eq. (5)). $H_2O_2$ can compensate for the $O_2$ lack and play a role as an external electron scavenger according to Eq. (6). It can trap the photogenerated conduction band electron and thus inhibiting the electron–hole recombination and producing hydroxyl radicals as shown by the Eq. (6).

$$TiO_2\, e^-_{(CB)} + O_2 \rightarrow O_2^{\bullet -} \quad (5)$$

$$e^-_{(CB)} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- \quad (6)$$

(ii) $H_2O_2$ may also be photolysed to produce hydroxyl radicals directly (Eq. (7)).

$$H_2O_2 \xrightarrow{h\nu} 2^{\bullet}OH \quad (7)$$

But the molar extinction coefficient of $H_2O_2$ at 254 nm is 19.6 $M^{-1}\,S^{-1}$. The applied wavelength in this work was 365 nm at which $H_2O_2$ has extremely low absorption. Hence, the oxidation of dye by photolysis of $H_2O_2$ (Eq. (7)) will be insignificant.

(iii) $H_2O_2$ also reacts with superoxide anion to form $^{\bullet}OH$ radical (Eq. (8)).

$$H_2O_2 + O_2^{\bullet -} \rightarrow {}^{\bullet}OH + H^+ + O_2 \quad (8)$$

At high $H_2O_2$ dosage (20 mM) the removal rate decreases due to:

(i) Hydroxyl radical scavenging effect of $H_2O_2$. The reaction between excess hydrogen peroxide and hydroxyl radical ($^{\bullet}OH$) forms hydroperoxy radical. These hydroperoxy radicals are much less reactive and do not contribute to oxidative degradation of dye (Eqs. (9) and (10)).

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (9)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad (10)$$

(ii) $H_2O_2$ is also a powerful hole scavenger [35]. In excess it may react with holes to produce oxygen and hydrogen ion (Eq. (11)). In photocatalytic degradation, hole oxidises the dye directly and with water produce hydroxyl radical. Hence, the removal of holes decreases the dye removal rate.

$$H_2O_2 + h_{VB}^+ \rightarrow O_2 + 2H^+ \quad (11)$$

### 3.7.2. Effect of $S_2O_8^{2-}$ addition

The effect of addition of $S_2O_8^{2-}$ on the photocatalytic oxidation of RY14 has been investigated by varying the amount of $(NH_4)_2S_2O_8$ from 1 to 4 g/l. The results are shown in Fig. 14. Addition of 1–3 g/l of $(NH_4)_2S_2O_8$ increases the decolourisation from 83.4 to 92.9% in 10 min and degradation from 75.5 to 86.7% in 20 min. Further increase in the addition increases the

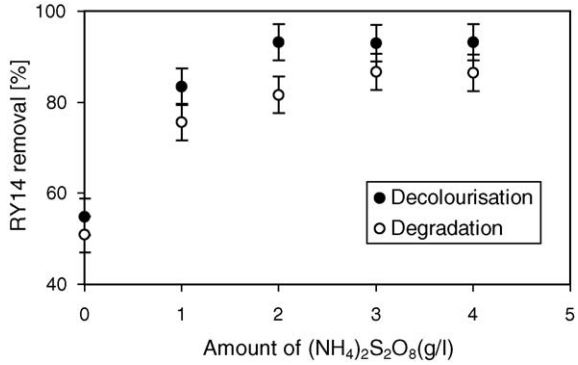


Fig. 14. Effect of $S_2O_8^{2-}$ addition on the decolourisation and degradation of RY14. $TiO_2$-P25 = 4 g/l, [RY14] = $5 \times 10^{-4}$ mol/l, pH 5.5 ± 0.1, irradiation time—decolourisation = 10 min, degradation = 20 min.

decolourisation by 2.7% and degradation by 1.0%. Our results are in good agreement with earlier results [17,33,36]. Addition of persulphate to photocatalytic processes enhances the decolourisation rate by three ways:

(i) Persulphate ion scavenges the conduction band electron and promotes the charge separation and production of other oxidising species namely sulphate radical anion (Eq. (12)).

$$S_2O_8^{2-} + e^-_{(CB)} \rightarrow SO_4^{\bullet -} + SO_4^{2-} \quad (12)$$

(ii) $S_2O_8^{2-}$ can generate sulphate radical anion ($SO_4^{\bullet -}$) both thermally and photolytically in aqueous solution. This radical anion is a strong oxidant and participates in the degradation processes by the following ways (Eqs. (13) and (14)):

$$SO_4^{\bullet -} \rightarrow e^-_{(CB)} \rightarrow SO_4^{2-} \quad (13)$$

$$SO_4^{\bullet -} \rightarrow H_2O \rightarrow {}^{\bullet}OH + SO_4^{2-} + H^+ \quad (14)$$

$$SO_4^{\bullet -} \rightarrow RY14 \rightarrow SO_4^{2-} + \text{Dye intermediate}$$

$$SO_4^{\bullet -} \rightarrow \text{Dye intermediate} \rightarrow \text{mineralisation.}$$

At high dosage of $S_2O_8^{2-}$ the inhibition of reaction occurs due to the increase in concentration of $SO_4^{2-}$ ion (Eq. (12)). The excess of $SO_4^{2-}$ ion is adsorbed on the $TiO_2$ surface and reduces the catalytic activity. The adsorbed $SO_4^{2-}$ ion also reacts with photogenerated holes (Eq. (15)) and with hydroxyl radicals (Eq. (16)).

$$SO_4^{2-} + h_{VB}^+ \rightarrow SO_4^- \quad (15)$$

$$SO_4^{2-} + {}^{\bullet}OH \rightarrow SO_4^{\bullet -} + OH^- \quad (16)$$

Since sulphate radical anion is less reactive than $^{\bullet}OH$ radical and $h^+$ the excess $SO_4^{2-}$ reduces the photooxidation of the dye.

### 3.7.3. Effect of $BrO_3^-$ addition

$BrO_3^-$ ion is an efficient electron acceptor and used as an additive to enhance photocatalytic degradation rate [17,33,36]. The effect of addition of $KBrO_3$ (1–4 g/l) on the photocatalytic decolourisation and degradation are shown in Fig. 15. The addition of $KBrO_3$ from 1 to 3 g/l increases the decolourisation from

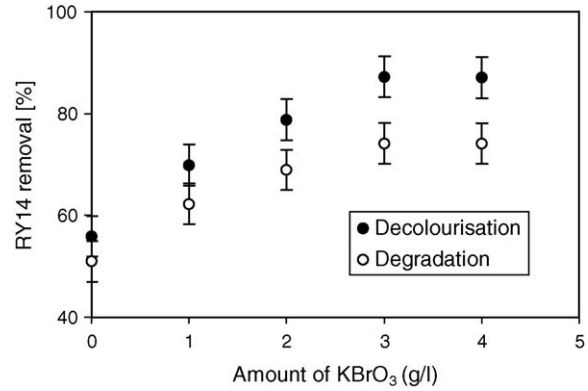


Fig. 15. Effect of $BrO_3^-$ addition on the decolourisation and degradation of RY14. $TiO_2$-P25 = 4 g/l, [RY14] = $5 \times 10^{-4}$ mol/l, pH 5.5 ± 0.1, irradiation time—decolourisation = 10 min, degradation = 20 min.

69.8 to 87.2% at the time of 10 min and the degradation from 62.2 to 74.1% at the time of 20 min. On further increase of $KBrO_3$ from 3 to 4 g/l the removal rate is almost constant. The enhancement of the removal rate is due to its electron scavenging effect by the reaction between $BrO_3^-$ ion and conduction band electron (Eq. (17).

$$BrO_3^- + 6e^-_{(CB)} + 6H^+ \rightarrow Br^- + 3H_2O \quad (17)$$

On further increase of $KBrO_3$ addition only small enhancement was observed. This is due to adsorption effect of $Br^-$ ion on $TiO_2$ surface, which affects the catalytic activity of $TiO_2$.

### 3.8. Effect of inorganic ions addition

The other auxiliary chemicals such as sodium carbonate and sodium chloride are used in the dyeing process. $Na_2CO_3$ is added to adjust the pH of the dye bath, which is important in fixing the dye on the fabrics and in the fastness of colour. Sodium chloride is mainly used in dyeing process for the transfer of dyestuff to fabric. Therefore, the dye industry wastewater contains a considerable amount of carbonate and chloride ions. The effect of addition of $Na_2CO_3$ on the photocatalytic oxidation of RY14 is shown in Fig. 16. Increase in the $Na_2CO_3$ addition decreases the removal efficiency. Addition of 1–4 g/l $Na_2CO_3$ decreases

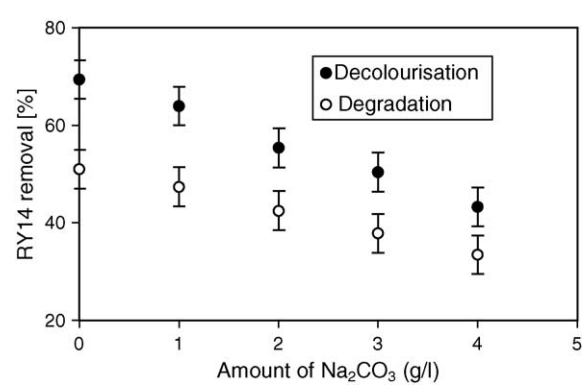


Fig. 16. Effect of $CO_3^{2-}$ ion addition on the decolourisation and degradation of RY14. $TiO_2$-P25 = 4 g/l, [RY14] = $5 \times 10^{-4}$ mol/l, pH 5.5 ± 0.1, irradiation time = 20 min.

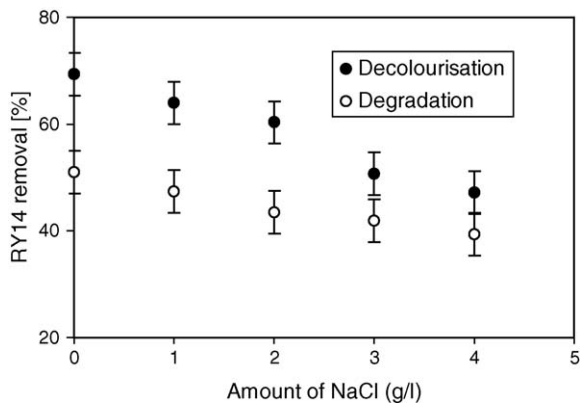


Fig. 17. Effect of $Cl^-$ ion addition on the decolourisation and degradation of RY14. $TiO_2$-P25 = 4 g/l, [RY14] = $5 \times 10^{-4}$ mol/l, pH 5.5 ± 0.1, irradiation time = 20 min.

the removal from 63.9 to 43.2% for decolourisation and 47.3 to 33.4% of degradation at the time of 20 min. The decrease in the degradation efficiency of the dye is due to hydroxyl radical scavenging property of carbonate ion as shown in the following Eqs. (18) and (19):

$$CO_3^{2-} + {}^{\bullet}OH \rightarrow OH^- + CO_3^{\bullet -} \quad (18)$$

$$HCO_3^- + {}^{\bullet}OH \rightarrow H_2O + CO_3^{\bullet -} \quad (19)$$

Thus, the primary oxidant hydroxyl radical decreases gradually with the increase in carbonate ion and consequently there is a significant decrease in photocatalytic oxidation. The influence of $Cl^-$ ion on the photocatalytic oxidation of RY14 has been studied using NaCl. The results are shown in Fig. 17. Increase of the addition of NaCl up to 4 g/l to the reaction solution decreases the decolourisation from 63.9 to 57.1% and degradation from 47.3 to 40.3% at the time of 20 min. The decrease in degradation efficiency in the presence of chloride ion is due to its hole and hydroxyl radical scavenging effects (Eqs. (20–23)) [29]

$$Cl^- + h_{VB}^+ \rightarrow Cl^{\bullet} \quad (20)$$

$$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet -} \quad (21)$$

$${}^{\bullet}OH + Cl^- \leftrightarrow HOCl^{-\bullet} \quad (22)$$

$$HOCl^{\bullet -} + H^+ \rightarrow Cl^{\bullet} + H_2O \quad (23)$$

The reaction of dye molecule with the hole has to compete with this reaction (Eq. (20)). The chloride radical anions formed can also block the reactive sites of the catalyst surface. The inhibiting effect of $CO_3^{2-}$ ion is greater than that of $Cl^-$ ion.

## 4. Conclusions

The RY14 is easily degraded by $TiO_2$-P25 assisted photocatalysis in aqueous dispersion under irradiation by UV-A radiation. The dye is resistant to direct photolysis. The optimum physico-chemical conditions for the efficient photooxidation of $5 \times 10^{-4}$ mol/l dye solution at room temperature were found to be: $TiO_2$-P25 concentration 4 g/l; radiation intensity 32 W; initial $H_2O_2$ concentration 15 mM; initial $(NH_4)_2S_2O_8$ concentration 3 g/l; initial $KBrO_3$ concentration 3 g/l. The photocatalytic decolourisation and degradation obey pseudo-first order kinetics at low initial concentrations. The initial decolourisation and degradation rates could be fitted to empirical Langmuir–Hinshelwood equation up to $3 \times 10^{-4}$ mol/l.

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